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DERWENT-WEEK: 199523

TITLE: Substrate **doping** method - involving formation of epitaxial film on substrate by irradiating its surface with **electromagnetic wave** and simultaneously supplying di:silane gas and deca borane gas

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PRIORITY-DATA: 1993JP-0256338 (September 21, 1993)

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ABSTRACTED-PUB-NO: JP 07094427A

BASIC-ABSTRACT:

The doping method uses a chamber (2) in which a Si substrate (3) is held by a stage (3a). A disilane gas and a deca borane gas are supplied to a Si substrate surface through nozzles (7,11) respectively.

Simultaneously,
synchrotron emission light (14) is irradiated on the Si substrate surface.
This enables formation of an epitaxial film on the substrate. The energy of this **electromagnetic wave** is more than the optical ionization energy of the **doping** gases.

ADVANTAGE - Makes it possible to carry out doping even at low temperature of 400 deg centigrade or less. Controls depth distribution and density in Si epitaxial film, precisely.

CHOSEN-DRAWING: Dwg.1/4

TITLE-TERMS: SUBSTRATE DOPE METHOD FORMATION EPITAXIAL FILM SUBSTRATE IRRADIATE SURFACE ELECTROMAGNET WAVE SIMULTANEOUS SUPPLY DI SILANE GAS DECA BORANE GAS

DERWENT-CLASS: L03 U11

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SECONDARY-ACC-NO:
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Notes:
1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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FULL CONTENTS

[Claim(s)]
[Claim 1] The doping gas used as one doping material of a composition element is introduced into the growth interior of a room which is growing up the epitaxial film on a substrate. The doping method characterized by irradiating the electromagnetic waves of the energy more than the photoionization energy of said doping gas at the doping gas on said substrate, and doping said doping material in said epitaxial film.
[Claim 2] The doping method characterized by controlling while doping the amount of irradiation of said electromagnetic wave in the doping method according to claim 1.
[Claim 3] The doping method by which it is performing [with the molecular beam which can be obtained from the solid of said atom]-in doping method Claim 1 or given in two-supply of atom for growth of said epitaxial film characterized.

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to the doping method which carries out impurities introduction, when forming an epitaxial film on a substrate -- it is.
[0002]
[Description of the Prior Art] For realization of the next-generation semiconductor device which aims at super-high accumulation and ultra high-speed, it is becoming indispensable to realize more detailed element structure in recent years. For that, the impurities diffusion and substance diffusion between semiconductor device structures become indispensable [very few low-temperature single crystal growing-up methods]. From this viewpoint, the silicon gas source molecular beam growing-up method using Silang system gas is studied briskly (for example, journal OBU Crystal Glaus, such as H.Hirayama 1990 volume [105th] 46 - 51

pages).

[0003] This method is explained briefly hereafter. The molecule of Silang system gas causes a dissociative adsorption reaction on Si board in a high vacuum container. This dissociative adsorption happens with the dangling bond which exists on Si surface. If the temperature of Si board to which the Silang system gas molecule stuck shall be 400 degrees or more, only Si atom will be left behind on Si board in the Silang system gas molecule to which it stuck, and epitaxial growth of Si will be attained. This is 400 degrees or more in temperature, and is because the hydrogen atom in the Silang system gas molecule which carried out dissociative adsorption turns into a hydrogen molecule and is desorbed from the substrate surface.

[0004] In the gas source molecular beam growing-up method as shown above, when doping impurities to the epitaxial growth layer which forms membranes, the method of supplying simultaneously with Silang system gas the doping gas which consists of a compound of an impurities atom on Si board is taken. That is, an impurities atom is introduced into the epitaxial layer grown up using the dissociative adsorption of the doping gas in Si board surface, and the thermal desorption of substances other than the impurities atom to dope. Therefore, according to the above method, temperature of Si board can be made low to Si to grow epitaxially and the minimum to which the thermal desorption of substances other than the impurities to dope happens.

[0005] For example, when doping a phosphorus (P) as impurities, HOSUFIN (PH3) is well used as source gas (doping gas) of this doping. Substances other than the impurities at this time are hydrogen. And when HOSUFIN is used as a P source of supply, carrying out temperature of Si board under low temperature to about 700 degrees C is realized.

[0006]

[Problem to be solved by the invention] However, in the case of the high-speed silicon bipolar transistor which has the working speed of 100GHz or more to which research and development are done briskly now, three or more [1019cm-] high-concentration B doping is needed at the thin base layer of 100nm or less which constitutes this. however, [the method using the dissociative adsorption of the impurities gas by heat which is the impurities doping method in the gas source molecular beam growing-up method mentioned above] A maximum will be decided by the amount of dissociative adsorption of doping gas [in / in the doping concentration of the impurities to the inside of grown-up Si epitaxial film / the substrate surface]. For this reason, if very high-concentration doping does not make temperature of a substrate high temperature very much, it is impossible, and only about [1018cm-] three doping concentration is obtained. That is, in the high-speed silicon bipolar transistor, even if it could thin-film-ize the base layer, high concentration doping of B required in order to realize high-speed operation was impossible.

[0007] Moreover, since the dissociative adsorption of gas is used for doping, you have to

perform doping concentration control by flux control of doping gas fundamentally. However, it is difficult to perform flux control of gas for a short time over the range of several figures moreover with high precision. For this reason, abnormal-conditions doping which doping concentration was changed in the depth direction a lot, and controlled impurities distribution with high precision was impossible, and, for this reason, application for the element for which abnormal-conditions doping of a quantum effect element etc. is needed by the conventional doping method was impossible.

[0008] Moreover, [in the case of the doping method by the gas source molecular beam growing-up method mentioned above, the dissociative adsorption of Silang system gas occurs at low temperature, but] Since a desorption process of hydrogen required in order that epitaxial growth may progress does not fully happen unless substrate temperature is about 400 degrees C or more, it cannot be 400 degrees C or less in substrate temperature theoretically. Therefore, when gallium with a large diffusion coefficient etc. is doped, diffusion into disorder and the oxide film of impurities distribution arises. That is, there was a problem that the thin film which has the precise impurities distribution by impurities with a large diffusion coefficient could not be formed.

[0009] This invention is made in order to cancel the above problems. In an epitaxially grown film, impurities can be doped to high concentration at low temperature, and it aims at enabling it to control impurities concentration and its depth direction distribution with high precision broadly in a grown-up epitaxial film moreover.

[0010]

[Means for solving problem] The doping method of this invention introduces the doping gas used as one doping material of a composition element into the growth interior of a room which is growing up the epitaxial film on a substrate. It is characterized by irradiating the electromagnetic waves of the energy more than the photoionization energy of doping gas at the doping gas on a substrate, and doping doping material in an epitaxial film.

[0011]

[Function] Doping gas decomposes by irradiating electromagnetic waves, doping material is generated, and it is doped by the epitaxial film with which this doping material is growing.

[0012]

[Working example] The composition of this invention is explained hereafter. In this invention, electromagnetic waves, such as vacuum purple outdoor daylight, are irradiated at doping gas, photoionization is started, and doping gas is ****(ed). That is, if the electromagnetic waves (vacuum purple outdoor daylight) of the energy more than photoionization energy are irradiated at doping gas, the molecule of doping gas will be ionized directly. When especially an inner shell electron is excited, two or more electron holes will be in the state of carrying out office ** on the bonding orbital of the molecule. And the molecule of doping gas is scatteringly

decomposed by the KURON restitution between these electron holes until it results in a single atom. As a result, the atom (impurities atom) of doping material is generated so much, and doping of an impurities atom progresses into the film which lay on the substrate as it is and is growing epitaxially. That is, doping of impurities can be advanced apart from epitaxial growth (Claim 1).

[0013] By the way, the maximum of the doping concentration to the inside of the silicon epitaxial film when not irradiating vacuum purple outdoor daylight is decided by the amount of dissociative adsorption on the surface of a substrate, and the amount of thermal desorption of atoms other than an impurities atom. The Silang system gas molecule causes [be / it / under / high vacuum container / setting] the dissociative adsorption reaction by heat on Si board, when substrate temperature is 400 degrees C or more. That is, by the molecular beam growing-up method which made Silang system gas source gas, in order to form the epitaxial layer of Si on Si board, Si board needs to be 400 degrees C or more.

[0014] Therefore, when the heat dissociation of atoms other than the impurities atom which is 400 degrees C or more, and dopes Si substrate temperature considers it as the temperature which hardly happens, it compares with the epitaxial amount of growth of Si. Since there is little amount of supply of the impurities atom by the heat dissociation of doping gas, only very low doping concentration is obtained. This means that the doping concentration of the impurities atom to the inside of a silicon epitaxial film differs greatly in the case where it is not considered as the case where vacuum purple outdoor daylight is irradiated. And it is possible to make it change continuously from concentration with high doping concentration to low concentration within the limits of this big doping concentration difference by controlling the light response by irradiating this vacuum purple outdoor daylight (Claim 2). To be shown in the working example 2 mentioned later, by controlling the amount of optical irradiation per unit time, a light response is controlled by this invention and the doping concentration to the inside of the epitaxial growth film of an impurities atom is promptly controlled with sufficient accuracy by it in the large range.

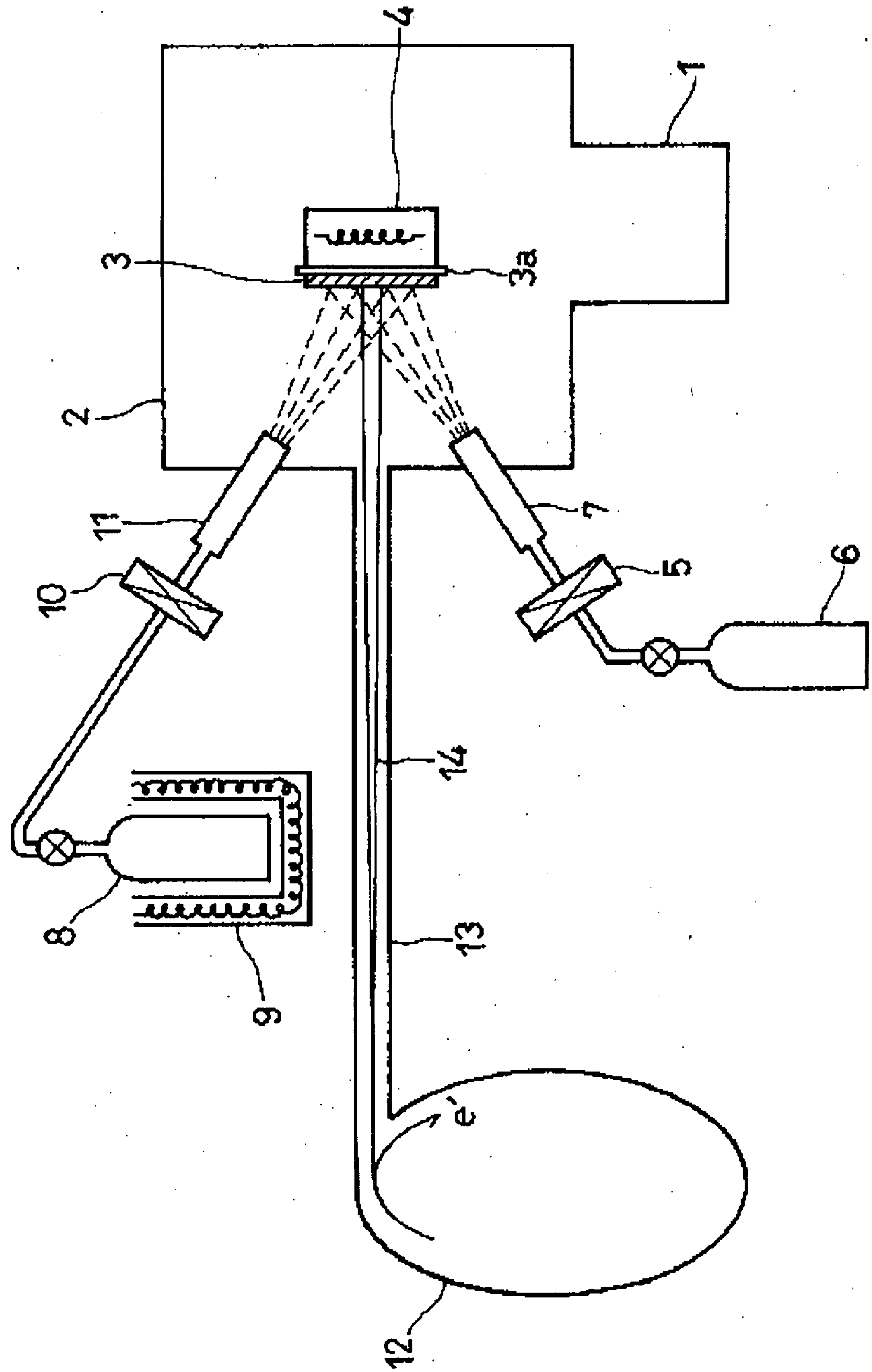
[0015] By the way, in supplying the silicon to grow epitaxially by Silang system gas, in substrate temperature, heat growth of a silicone film does not take place below 400 degrees C. Thus, if doping by this invention is performed when substrate temperature is 400 degrees C or less, supply of a up to [the substrate of Si atom for epitaxial growth] will also be depended on light excitation decomposition of the Silang system gas by irradiation of the vacuum purple outdoor daylight by synchrotron radiation etc. For this reason, if the amount of optical irradiation per unit time is controlled, the growth rate of Si epitaxial film also changes with the amount of generation of an impurities atom, and doping concentration of an impurities atom cannot be controlled by such a state. That is, when performing epitaxial growth of Si by the supply of Si by decomposition of Silang system gas, substrate temperature cannot be lowered

if it is going to control doping concentration.
[0016] On the other hand, silicon growth can be caused regardless of the thermal desorption from the substrate of optical irradiation or hydrogen by supplying silicon using a silicon solid source (Claim 3). Therefore, since it becomes constant [the growth rate of silicon / related always] to optical irradiation even if substrate temperature is 400 degrees C or less, it becomes possible by controlling the amount of optical irradiation per unit time to control doping concentration with sufficient accuracy in the large range promptly.
[0017] One working example of this invention is explained with reference to a figure below. Working example 1. drawing 1 is the cross-sectional composition figure showing the composition of the equipment for realizing one working example of this invention. This working example 1 explains the case where the silicon with which the continuation irradiation of the vacuum purple outdoor daylight was carried out, and B was introduced into it while supplying Silang system gas and impurities gas to the silicon substrate is grown epitaxially. Moreover, decaborane (B10H14) is used as impurities gas here, using JISHIRAN (Si2H6) as Silang system gas.
[0018] Operation is explained hereafter. First, the Si board 3 is laid on the stage 3a in the growth room 2 linked to the vacuum exhaust air pump 1, subsequently the vacuum exhaust air of the inside of the growth room 2 sealed using the vacuum pump 1 is carried out, and it is considered as a predetermined degree of vacuum. Then, the Si board 3 is heated at 550 degrees C by the heating machine style 4, and by opening a valve 5 after this, from a nozzle 7, JISHIRANGASU with which the JISHIRAN cylinder 6 is filled up is introduced in the growth room 2, and is supplied on the Si board 3 surface. The amount of supply of JISHIRANGASU at this time was controlled so that the partial pressure in the growth room 2 was set to 1.5x10-4Torr.
[0019] By opening a valve 10, from a nozzle 11, the decaborane gas which occurred by on the other hand heating simultaneously the container 8 with which the decaborane solid is enclosed at heating machine guard 9 is introduced in the growth room 2, and is supplied to the Si board 3 surface. The amount of supply of decaborane gas was controlled so that the partial pressure in the growth room 2 served as the range of 4.0x10-8 - 4.0x10-6Torr. The synchrotron radiation 14 which occurred in the electronic accumulation ring 12 and was simultaneously introduced into the growth room 2 through the vacuum duct 13 at this time is irradiated at the decaborane gas on the Si board 3 surface. This synchrotron radiation 14 has a peak in 1000A in [wavelength] 30-1500A. Here, the amount of irradiation photons in the 3rd page of Si board was per second 2x1016 pieces.
[0020] As mentioned above, **** of decaborane gas can progress and B atom can make it generate in large quantities by irradiating the synchrotron radiation 14 at the decaborane gas put in in the growth room 2. And it is introduced into Si epitaxial film which is growing by this

generated B atom lying on the Si board 3 as it is, carrying out dissociative adsorption to a substrate 3 with heat, and being desorbed from hydrogen. Thus, in this working example 1, since the single atom B is generated so much by electronic excitation of decaborane by the synchrotron radiation (vacuum purple outdoor daylight) 14, high-concentration doping of an impurities atom is attained by it.

[0021] Drawing 2 is the correlation diagram having shown B concentration in Si epitaxial film to each partial pressure of the decaborane introduced into the growth room 2 by the "black dot." "With a circle [white]" showed the case where B in Si epitaxial film was introduced without irradiating the synchrotron radiation 14 for comparison. By the doping method of this working example, it turns out that doping concentration high 100 or more times is obtained as compared with the method of doping B by the conventional thermal cracking so that clearly from this result. And it turns out that about [1021cm-] three high-concentration impurities introduction is possible.

[0022] By the way, it was considered as the temperature to which the hydrogen desorption from the substrate temperature which carries out film formation does not take place, using decaborane as a source of supply of B which is JISHIRAN and an impurities atom as a source of Si to grow epitaxially, and the epitaxial growth and impurities introduction by irradiating vacuum purple outdoor daylight here were tried.



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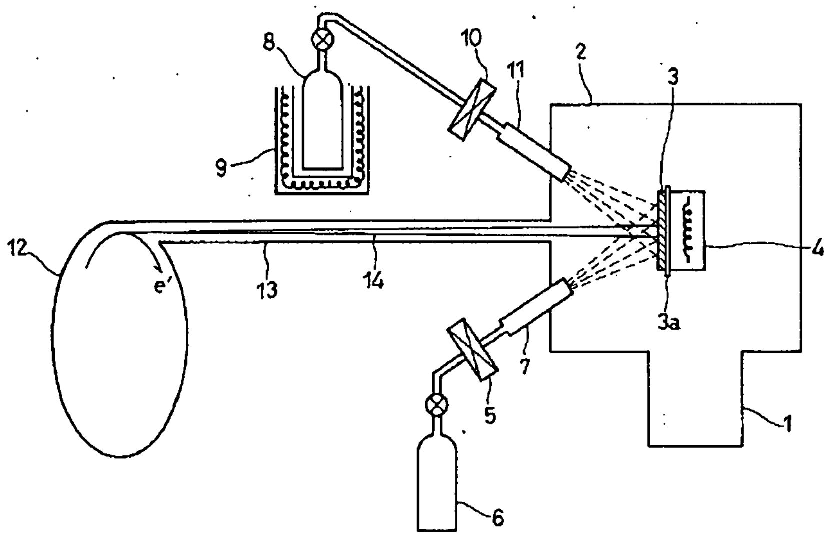
Drawing selection drawing 1



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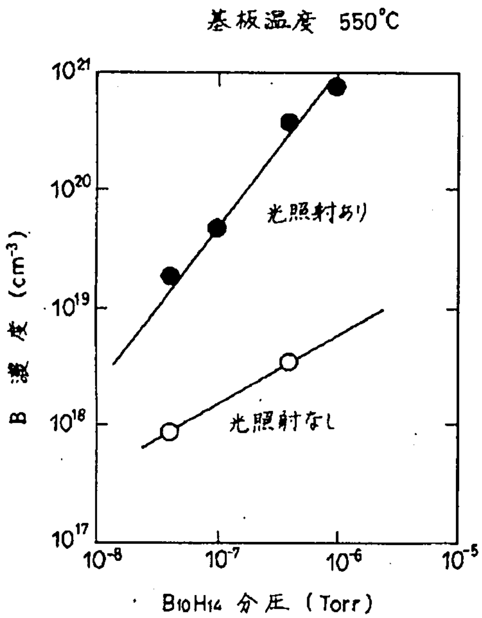

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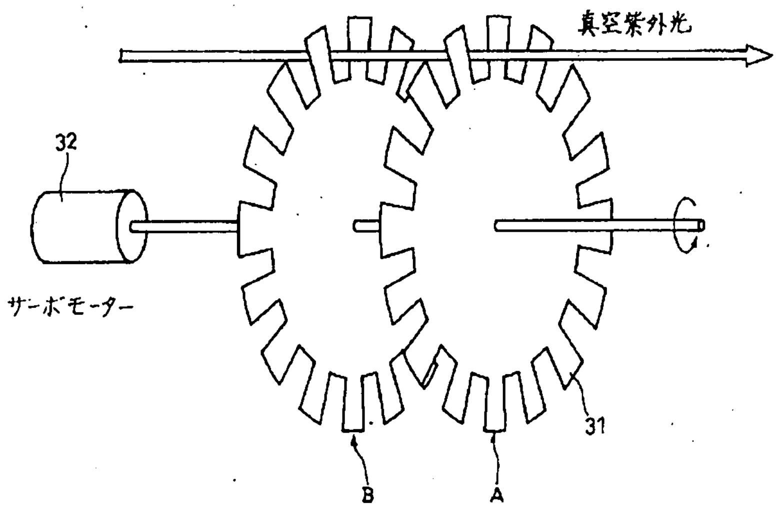

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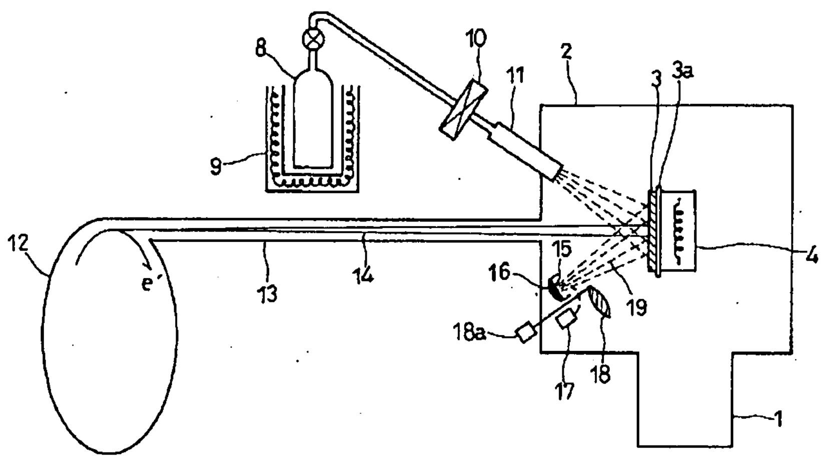

[Translation done.]